



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 2/50, G03F 7/031, C07D 335/16, 311/86, C07C 49/84		A1	(11) International Publication Number: WO 97/44364 (43) International Publication Date: 27 November 1997 (27.11.97)
(21) International Application Number: PCT/US97/08512 (22) International Filing Date: 19 May 1997 (19.05.97)		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(30) Priority Data: 60/017,127 20 May 1996 (20.05.96) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(71)(72) Applicants and Inventors: BOWERS, Joseph, Stanton, Jr. [US/US]; 63 South Georgia Avenue, Mobile, AL 36604 (US). NAGARAJAN, Rajamani [US/US]; 3230 Cumberland Road #14, Ocean Springs, MS 39564 (US). PITTMAN, Charles, Uriah, Jr. [US/US]; 18 Triangle Townhouses, Highway 25, Starkville, MS 39759 (US). JÖNSSON, E., Sonny [SE/SE]; Tomtebogatan 7II, S-103 39 Stockholm (SE).			
(74) Agents: SUMMA, Philip et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).			
(54) Title: PHOTOACTIVE COMPOUNDS FOR USE WITH NARROW WAVELENGTH BAND ULTRAVIOLET (UV) CURING SYSTEMS			
(57) Abstract			
<p>Novel substituted diaryl ketones, photopolymerization compositions including the compounds, and methods using the same are disclosed. Polymerization of compositions which include the compounds of the invention may be activated by irradiating the composition with ultraviolet light using conventional techniques and radiation sources to give greatly improved cure speeds. The compounds of the invention also show a significantly elevated level of reactivity at a narrow wavelength band, with a peak emission wavelength at or near 308 nm. Because of the increased level of activity, the photoinitiator can be used in considerably lower amounts.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

PHOTOACTIVE COMPOUNDS FOR USE WITH NARROW
WAVELENGTH BAND ULTRAVIOLET (UV) CURING SYSTEMS

Field of the Invention

This invention relates generally to novel photoactive compounds and methods for using and making the same. More particularly, this invention relates to 5 substituted diaryl ketones and methods of using the same in photoactivatable polymerization systems.

Background of the Invention

Ethylenically unsaturated compounds, and in particular acrylate derivatives, can be polymerized by 10 irradiation with ultraviolet light of wavelength between 200 and 450 nanometers (nm) in the presence of a bimolecular photoinitiating system. Typically, the photoinitiating system includes (1) a diaryl ketone photoinitiator and (2) a coinitiator or synergist, that 15 is, a molecule which serves as a hydrogen atom donor. The coinitiators or synergists are typically alcohols, tertiary amines or ethers which have available hydrogens attached to a carbon adjacent to a heteroatom.

-2-

Examples of commercially available diaryl ketone photoinitiators useful in bimolecular photoinitiator systems include benzophenone, 2,4-dimethylbenzophenone, isopropylthioxanthone, and 2,4-diethylthioxanthone. The UV absorption spectrum for these individual photoinitiators, however, do not match-up efficiently with the UV emission spectra of the standard commercially available mercury vapor bulbs.

10 Thus, commercially viable UV curing processes can require a relatively large amount of initiator and synergist incorporated into the formulation. This can lead to cured articles which contain high levels of residual photoinitiator and synergist, which in turn 15 can result in decreased light fastness and lower resistance to oxidative degradation. In addition, the residual photoinitiator and synergist can be extracted or leach out of the cured article or migrate to the surface of the article. Many times the physical 20 properties of the article are degraded by the presence of the residual photoinitiator and synergist.

Summary of the Invention

The present invention provides novel substituted diaryl ketones useful for photopolymerizing ethylenically unsaturated compounds. The novel 25 compounds of the invention are particularly useful for photopolymerizing acrylate derivatives by irradiation with ultraviolet light of wavelength between 200 and 450 nm in the presence of a coinitiator or synergist. 30 The present invention also provides photopolymerizable systems which include the novel diaryl ketone compounds of the invention as a component thereof, as well as methods for using the compounds of the invention in photopolymerization systems.

- 3 -

Brief Description of the Drawings

Some of the features and advantages of the invention having been described, others will become apparent from the detailed description which follows, 5 and from the accompanying drawings, in which:

Figure 1 illustrates the ultraviolet (UV) emission spectrum of an excimer lamp as described in U.S. Patent No. 5,504,391;

10 Figure 2 illustrates the UV absorption spectrum of 4,4'-bis(4-isopropylphenoxy)benzophenone;

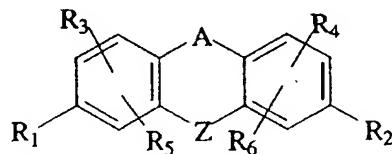
Figure 3 illustrates the UV absorption spectrum of 4,4'-bis(phenoxy)benzophenone;

Figure 4 illustrates the UV absorption spectrum of 4-(N-morpholino)benzophenone; and

15 Figure 5 illustrates the UV absorption spectrum of 4,4'-bis(2,4-di-tert-amylphenoxy)benzophenone.

Detailed Description of the Invention

Preferred diaryl ketones of the invention are appropriately substituted to possess UV spectra with significant absorption bands between 250 and 350 nanometers (nm), and more preferably between 290 and 325 nm. The novel compounds of the invention include substituted diaryl compounds according to Formula (I) 25 below:



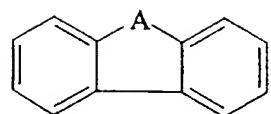
(I)

wherein:

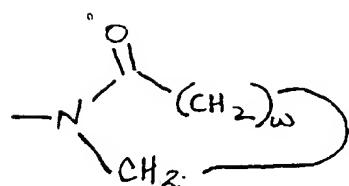
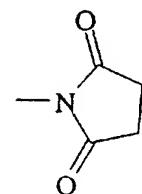
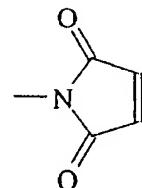
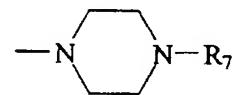
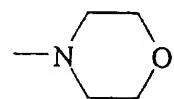
A is -CO- or -CO-CO-;

30 Z is (H,H), -CH₂-, -S-, -O-, -CO-, -NR₅-, or a bond bridging the two aromatic rings, i.e.,

- 4 -

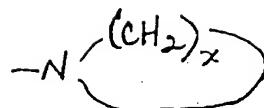


each R_1 and R_2 is independently selected from the group consisting of H,

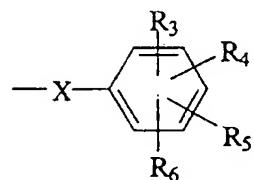
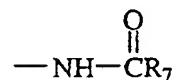
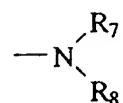


wherein $w = 2$ to 6

-5-



wherein x is 4 to 5



and

X-R_7 ;

X is O or S;

5 each R_3 , R_4 , R_5 , and R_6 is independently selected from the group consisting of -H, -Cl, -Br, -
 NO_2 , -CN, -OH, C1 to C8 alkyl, C6 to C8 aryl, C7 to C24 alkylaryl or arylalkyl, C1 to C8 alkoxy, C6 to C18 aryloxy, C7 to C24 alkylaryloxy or arylalkoxy, C1 to C8 alkylthioether, -COOH, and -COOR₇; and

10 each R_7 , R_8 and R_9 is independently selected from the group consisting of C1 to C8 alkyl and C7 to C24 alkylaryl or arylalkyl.

- 6 -

Exemplary compounds in accordance with Formula I include but are not limited to 4,4'-bis(4-isopropylphenoxy)benzophenone, 4,4'-bis(phenoxy)benzophenone, 4-(N-morpholino)benzophenone, 5 and 4,4'-bis(2,4-di-t-amylphenoxy)benzophenone.

Generally the compounds of Formula (I) can be prepared using techniques known in the art for preparing 4,4'-disubstituted diaryl ketones, and in particular 4,4'-diphenoxylbenzophenone, as well as other substituted diphenoxylbenzophenones. These processes are known in the open literature as well as the patent literature. For example, Crochemore (FR 2,617,160) teaches reacting diphenylether with substituted phenoxybenzoic acids in liquid HF at about 50°. Towle (EP 262,919) teaches reacting diphenylether and a substituted phenoxybenzoyl chloride in a chlorinated solvent in the presence of a Friedel-Crafts catalyst and a protic controlling agent to obtain better isomeric purity. Keller (U.S. Patent No. 3,366,691) teaches the preparation of diphenoxylbenzophenones by reacting diphenyl ethers with AlCl₃ and phosgene at about 80°C. Janson et al. (U.S. Patent No. 4,843,179) teaches reacting diphenyl ether with carbon dioxide under pressure at about 148°C in the presence of a promoting agent such as phosphoryl chloride. Each of the above Crochemore, Towle, Keller, and Janson references are incorporated in their entirety by reference.

In another embodiment of the invention, 30 photopolymerizable compositions are provided which include a compound of Formula (I) above as a photoinitiator. As used herein, and as will be appreciated by the skilled artisan, the term photopolymerizable composition refers to compositions 35 which harden or cure upon exposure to radiation.

Generally the compositions of the invention include ethylenically unsaturated compounds, including

monomers, oligomers, polymers, prepolymers, resinous materials, optionally dispersed or dissolved in a suitable solvent that is copolymerizable therewith, and mixtures thereof, which are photopolymerizable when 5 exposed to a source of UV radiation. As will be appreciated by the skilled artisan, the photopolymerizable compounds can be monofunctional, or can include two or more terminal polymerizable ethylenically unsaturated groupings per molecule.

10 Exemplary photopolymerizable compounds or precursors include, but are not limited to, reactive vinyl monomers, including acrylic monomers, such as acrylic and methacrylic acids, and their amides, esters, salts and corresponding nitriles. Suitable 15 vinyl monomers include, but are not limited to, methyl acrylate, ethyl acrylate, n- or tert-butylacrylate, isooctyl acrylate, methyl methacrylate, ethylmethacrylate, 2-ethylhexyl methacrylate, butylacrylate, isobutyl methacrylate, the corresponding 20 hydroxy acrylates, i.e., hydroxy ethylacrylate, hydroxy propylacrylate, hydroxy ethylhexyl methacrylate, glycol acrylates, i.e., ethylene glycol dimethacrylate, hexamethylene glycol dimethacrylate, the allyl acrylates, i.e., allyl methacrylate, diallyl 25 methacrylate, the epoxy acrylates, i.e., glycidyl methacrylate, and the aminoplast acrylates, i.e., melamine acrylate. Others such as vinyl acetate, vinyl and vinylidene halides and amides, i.e., methacrylamide, acrylamide, diacetone acrylamide, 30 butadiene, styrene, vinyl toluene, and the like are also included. Prepolymers include acrylated epoxides, polyesters and polyurethanes, and are typically combined with a suitable monomer for viscosity control. The photopolymerizable compounds may be polymerized to 35 form homopolymers or copolymerized with various other monomers.

The photoinitiator is present in the photopolymerizable composition in an amount sufficient to initiate polymerization of photopolymerizable compounds therein upon exposure to ultraviolet radiation. One advantage of the compounds of the invention is the decreased amounts required to initiate polymerization in comparison to conventional photoinitiators. The composition can include about 0.001 to about 10 percent by weight photoinitiator, preferably about 0.005 to about 0.10, based on the total weight of the photopolymerizable compounds.

It can be advantageous to also include as a component of the compositions a coinitiator or synergist, that is, a molecule which serves as a hydrogen atom donor. Coinitiators or synergists are known in the art, and are typically alcohols, tertiary amines or ethers which have available hydrogens attached to a carbon adjacent to a heteroatom. Such co-initiators are typically present in an amount of about 0.2 to about 25 percent by weight based on the total weight of the composition. Suitable compounds include triethanolamine, methyl-diethanolamine (MDEA), ethyldiethanolamine and esters of dimethylamino benzoic acid. These compounds behave as co-initiators or accelerators for the primary photoinitiators and can increase the efficiency and speed of the polymerization process.

In addition, the photopolymerizable compositions may contain polymerization inhibitors, fillers, ultraviolet absorbers and organic peroxides.

The photopolymerizable compositions can be applied or deposited on a surface of a substrate using conventional techniques and apparatus. The composition can be applied as a substantially continuous film; alternatively, the composition can be applied in a discontinuous pattern. Usually the compositions of the

invention are fluid at ordinary operating temperatures (between ambient and up to about 60°C).

5 The thickness of the deposited composition can vary, depending upon the desired thickness of the resultant cured product. Advantageously, the composition is applied to the substrate surface in an amount sufficient to provide a cured coating having a thickness between about 1 micron and about 5 mils.

10 Typically, the substrate is coated with the uncured photopolymerizable composition and passed under a ultraviolet providing light beam by a conveyer moving at predetermined speeds. The substrate to be coated can be, for example, metal, wood, mineral, glass, paper, plastic, fabric, ceramic, and the like.

15 The active energy beams used in accordance with the present invention may be visible light or ultraviolet light or may contain in their spectra both visible and ultraviolet light. The polymerization may be activated by irradiating the composition with 20 ultraviolet light using any of the techniques known in the art for providing ultraviolet radiation, i.e., in the range of 200 nm and 450 nm ultraviolet radiation. The radiation may be natural or artificial, monochromatic or polychromatic, incoherent or coherent 25 and should be sufficiently intense to activate the photoinitiators of the invention and thus the polymerization. Conventional radiation sources include fluorescent lamps, mercury, metal additive and arc lamps. Coherent light sources are the pulsed nitrogen, 30 xenon, argon ion- and ionized neon lasers whose emissions fall within or overlap the ultraviolet or visible absorption bands of the compounds of the invention.

35 As noted above, preferably the diaryl ketones of the invention are appropriately substituted to possess UV spectra with significant absorption bands between 250 and 350 nm and in particular between 290

-10-

and 325 nm. Accordingly, the compounds can be irradiated with a narrow wavelength band, high pressure fill UV curing lamp known as an excimer lamp with spectral emphasis in the 250 to 350 nm range, and in 5 particular with its peak emission wavelength at or near 308 nm, as described in U.S. Patent No. 5,504,391, the entire disclosure of which is hereby incorporated in its entirety. The compounds of Formula (I) show a significantly elevated level of reactivity at these 10 wavelengths. Because of the increased level of activity the photoinitiator can be used in considerably lower amounts.

When polymerized by exposure to UV radiation, the compositions can give a substantially tack-free 15 product which is durable for ordinary handling. The compositions are useful in any of the types of applications known in the art for photopolymerizations, including as a binder for solids to yield a cured product in the nature of a paint, varnish, enamel, 20 lacquer, stain or ink. The compositions are particularly useful in the production of photopolymerizable surface coatings in printing processes, such as lithographic printing, screen printing, and the like.

25 The present invention will be further illustrated by the following non-limiting examples.

Example 1

Synthesis of 4,4'-Dibromobenzophenone

30 4,4'-Dibromobenzophenone, a tuned photoinitiator precursor, can be prepared by the ambient temperature reaction of p-bromobenzoyl chloride with bromobenzene, catalyzed by anhydrous aluminum chloride. This preparation is described by W.J. Leigh et al., Can. J. Chem., 58, 1980, pp. 2537-2549.

-11-

Example 2

Synthesis of 3,6-Dibromoanthrone

3,6-Dibromoanthrone, a tuned photoinitiator precursor, can be prepared by first producing 2,7-dibromoanthraquinone by the direct bromination of anthraquinone with elemental bromine under pressure at about 160°C as described by Diehl, *Chem. Ber.*, 11, 1878, p181. The dibromoanthraquinone is then reduced to the 3,6-dibromoanthrone with aluminum metal and sulfuric acid as described by R. Biehl, et al., *J. Amer. Chem. Soc.*, 99(13), 1977, pp.4278-4286.

Example 3

Synthesis of 2,7-Dibromoxanthone

2,7-Dibromoxanthone, a tuned photoinitiator precursor, can be prepared by the direct bromination of xanthone using elemental bromine with a trace of iodine as catalyst in, acetic acid at about 100°C. This preparation is described by P.R.J. Gaffney et al., *J. Chem. Soc., Perkin Trans. 1*, 1991(6), pp.1355-1360.

The 2,7-Dibromoxanthone can also be prepared by the phosgenation of 4,4'-dibromo-diphenyl ether using aluminum chloride as catalyst. This process is described in U.S. Patent 2,776,299.

Example 4

Synthesis of 2-Aminothioxanthone

Thiosalicyclic acid (6 g.) was dissolved in 200 g. of 98% sulfuric acid and cooled to 5°C for 16 hours and then quenched into ice water. The precipitate was stirred with 5% aqueous caustic for 2 hours, filtered, and washed with water. The precipitate was then stirred with 50/50 acetonitrile/acetone to remove unreacted acetanilide. The resulting product was hydrolyzed in 70% sulfuric acid at 80-105°C for 8 hours to give after neutralization, washing and drying 2-aminothioxanthone.

-12-

a tuned photoinitiator precursor, mp 227-229°C.
Structure was confirmed by IR, NMR, C-13 NMR and MS.

Example 5

Synthesis of 2, Morpholinothioxanthone

5 2-Aminothioxanthone (4.9 g.), anhydrous potassium carbonate (4.5 g.) and di(ethylene-glycol) diethyl ether (150 ml) were heated to reflux (180°C) and 5.2 g. of 2-bromoethyl ether was added. The reaction was held at reflux for 24 hours, filtered hot
10 and the solvent removed under vacuum. The residue was recrystallized from acetone to give 2-morpholinothioxanthone, mp 166-167°C. Structure was confirmed by IR, NMR, C-13 NMR and MS.

Example 6

15 **Synthesis of Michler's Ketone Type Compounds**

Michler's Ketone type compound such as p,p'-dicyclobutylaminobenzophenone can be prepared by reacting about 4.3 molar equivalents of N-phenylcyclobutylamine with one molar equivalent of phosgene at
20 under 24°C to form the 4-cyclobutylamino-benzoyl chloride. The addition of the ZnCl₂ completes the reaction to produce the desired compound. This process is described in U.S. Patent 2,882,472.

Example 7

25 **Synthesis of 4,4'-bis(4-Isopropylphenoxy)benzophenone**

To a solution of 4-isopropylphenol (20.4 g.) in 30 ml of dimethylformamide was added slowly a slurry of sodium hydride, 60% in mineral oil (6.0 g.) in 150 ml of dimethylformamide. When the reaction was
30 complete, 8.5 g. of 4,4'-dibromobenzophenone and 1.0 g. dendritic copper powder were added and the reaction mixture heated to reflux and held at reflux for 24 hours. The solvent was removed under vacuum and the residue poured into ice-water. The crude product was

-13-

recrystallized from ethanol to give the desired compound, mp 104-105°C. Structure was confirmed by IR, NMR, C-13 NMR and MS.

Example 8

5 Synthesis of 4,4'-bis[2,4-di(1,1-Dimethylpropyl)phenoxy]benzophenone

The same process as example 7 was followed except that di-tert-amylphenol was used in place of 4-isopropylphenol. After recrystallization from ethanol 10 the desired compound was obtained, mp 54-56°C. Structure was confirmed by IR, NMR, C-13 NMR and MS.

Example 9

Synthesis of 4-Morpholinobenzophenone

15 4-Morpholinobenzophenone was found commercially available from Aldrich Chemical Co.

Example 10

Synthesis of 4,4'-Diphenoxylbenzophenone

Diphenoxylbenzophenone can be prepared by the aluminum chloride catalyzed reaction between diphenyl 20 ether and phosgene over about 3 hours at 80°C and 45 psig pressure. The resulting product has a mp 146-147°C. This process is described in U.S. Patent 3,366,691. We prepared 4,4'-diphenoxylbenzophenone by the same procedure used in Example 7 to prepare 4,4'-bis(4-isopropylphenoxy)benzophenone, except that phenol 25 was used in place of 4-isopropyl-phenol. The mp of the product compound agreed with the literature and the structure was confirmed by IR, NMR, C-13 NMR and MS.

Example 11

30 Synthesis of 3,6-Diphenoxanthrone Derivatives

Starting with 3,6-dibromoanthrone, diphenoxanthrone derivatives could be prepared by one skilled in the art using the same process as Example 7, except that 3,6-dibromoanthrone is used in place of

-14-

4,4'-dibromobenzophenone and the appropriate phenol is used in place of 4-isopropylphenol.

Example 12

A resin blend was prepared from 501 grams polyester polyol derivative sold under the name EB80 from UCB Radcure, 120 grams glyceryl propoxy triacrylate sold under the name OTA-480, and 250 grams tripropylene glycol diacrylate. This blend was used for all photopolymerizations. Methyldiethanolamine, MDEA, was added to a portion of the blend to provide 1.5 weight percent MDEA. The photoinitiators were added in the amounts shown in tables 1 and 2, and the mixtures were applied to provide 2 mil films on paper panels. The paper panels were passed under an excimer lamp which has a peak emission wavelength at or near 308 nm. For comparison the paper panels were also passed under a medium pressure mercury lamp. Both lamps were set for 400 watts per inch. Cure speeds were determined as the maximum belt speed at which the film passed the thumb twist test, and are given in the following tables.

Table 1

Initiator	Cure Speed (Feet per minute)	Concentration of photoinitiator for Medium Pressure Mercury Lamp (Wt. %)	Concentration of photoinitiator for Excimer Lamp (Wt. %)
Benzophenone	150	1.5	-
25 4,4'-Bis(4-isopropylphenoxy)benzophenone	270	0.04	0.01
4,4'-Bis(phenoxy)benzophenone	425	0.053	0.013
4-(N-Morpholino)benzophenone	325	0.02	0.007
4,4'-Bis(2,4-di-t-amylphenoxy)benzophenone	325	0.056	0.011

-15-

Table 2

Initiator	Concentration of photoinitiator (Wt. %)	Cure Speed for Medium Pressure Mercury Lamp (Feet per minute)	Cure Speed for Excimer Lamp (Feet per minute)
Benzophenone	1.5	150	290
4,4'-Bis(4-isopropylphenoxy)benzophenone	0.04	270	>590
5 4,4'-Bis(phenoxy)benzophenone	0.053	425	>590
4-(N-Morpholino)benzophenone	0.02	325	>590
4,4'-Bis(2,4-di-t-amylphenoxy)benzophenone	0.055	325	>590

10 The results in Table 1 show that when the compounds of the invention are used with an excimer lamp versus a medium pressure mercury lamp that only about one-fourth of the amount of photoinitiator is required to give equivalent cure speeds.

15 The results in Table 2 show that when the same concentration of photoinitiator is used with both an excimer and a medium pressure mercury lamp that the excimer lamp provides greatly increased cure speeds.

20 Both tables show that the compounds of the invention provide cure speeds much higher than does benzophenone.

UV Spectra are provided for the excimer lamp, and for the four compounds of the invention used in the example, 4,4'-bis(4-isopropylphenoxy)benzophenone, 4,4'-bis(phenoxy)benzophenone, 4-(N-morpholino)benzophenone, and 25 4,4'-bis(2,4-di-t-amylphenoxy)benzophenone in Figures 1, 2, 3, 4, and 5, respectively.

The foregoing examples are illustrative of the present invention and are not to be construed as limiting thereof. The invention is defined by the

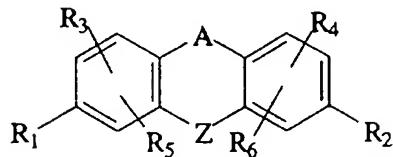
-16-

following claims, with equivalents of the claims to be included therein.

-17-

THAT WHICH IS CLAIMED IS:

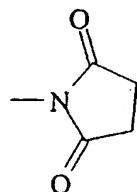
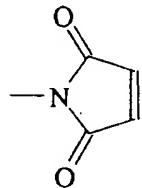
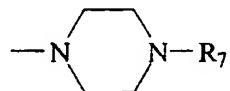
1. A compound having the Formula (I):



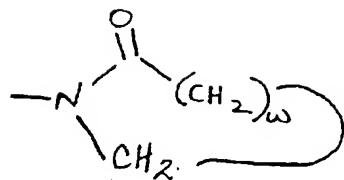
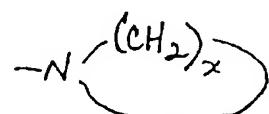
(I)

wherein:

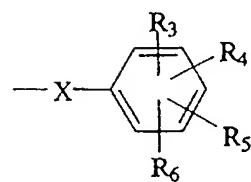
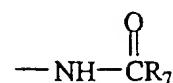
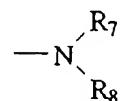
A is -CO- or -CO-CO-;

5 Z is (H,H), -CH₂-, -S-, -O-, -CO-, -NR₉-, or a bond bridging the two aromatic rings,each R₁ and R₂ is independently selected from the group consisting of H,

- 18 -

wherein $w = 2$ to 6

10

wherein x is 4 to 5

and

$X-R_7$, with the proviso that both R_1 and R_2 are not H;

X is O or S;

-19-

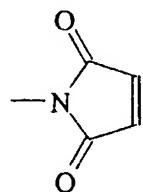
15 each R₃, R₄, R₅, and R₆ is independently selected from the group consisting of -H, -Cl, -Br, -NO₂, -CN, -OH, C1 to C8 alkyl, C6 to C8 aryl, C7 to C24 alkylaryl or arylalkyl, C1 to C8 alkoxy, C6 to C18 aryloxy, C7 to C24 alkylaryloxy or arylalkoxy, C1 to C8 alkylthioether, -COOH, and -COOR₇; and

20 each R₇, R₈ and R₉ is independently selected from the group consisting of C1 to C8 alkyl and C7 to C24 alkylaryl or arylalkyl.

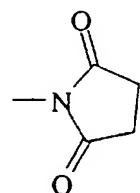
2. The compound of Claim 1, wherein at least one of R₁ and R₂ is



3. The compound of Claim 1, wherein at least one of R₁ and R₂ is

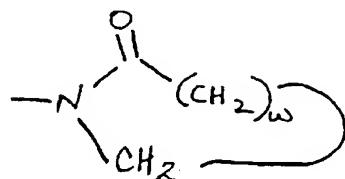


4. The compound of Claim 1, wherein at least one of R₁ and R₂ is



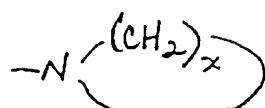
- 20 -

5. The compound of Claim 1, wherein at least one of R_1 and R_2 is



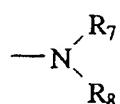
wherein $w = 2$ to 6

6. The compound of Claim 1, wherein at least one of R_1 and R_2 is

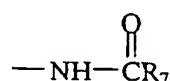


wherein x is 4 to 5

7. The compound of Claim 1, wherein at least one of R_1 and R_2 is

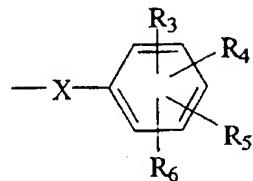


8. The compound of Claim 1, wherein at least one of R_1 and R_2 is



-21-

9. The compound of Claim 1, wherein at least one of R₁ and R₂ is



10. The compound of Claim 1, wherein at least one of R₁ and R₂ is X-R₁.

11. The compound of Claim 1, wherein A is -CO-.

12. The compound of Claim 1, wherein Z is (H, H).

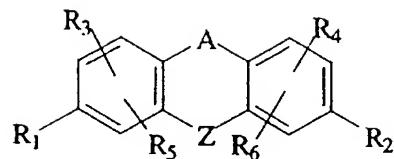
13. The compound of Claim 1, wherein said compound is 4,4'-bis(4-isopropylphenoxy)benzophenone

14. The compound of Claim 1, wherein said compound is 4,4'-bis(phenoxy)benzophenone.

15. The compound of Claim 1, wherein said compound is 4,4'-bis(2,4-di-t-amylphenoxy)benzophenone.

16. A photopolymerizable composition comprising a photopolymerizable compound comprising at least one ethylenically unsaturated double bond and a photoinitiator having the Formula (I)

- 22 -



5

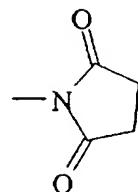
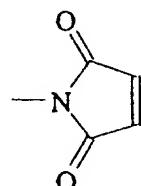
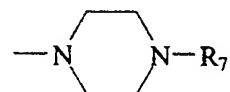
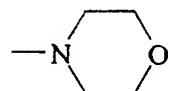
wherein:

(I)

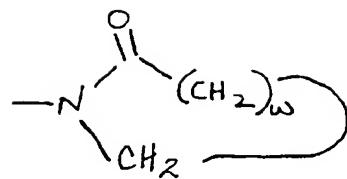
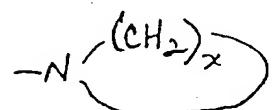
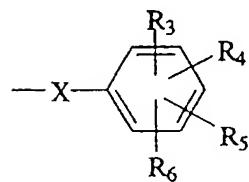
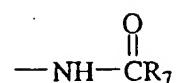
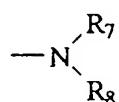
A is -CO- or -CO-CO-;

Z is (H, H), -CH₂-, -S-, -O-, -CO-, -NR₉-, or a bond bridging the two aromatic rings,

10

each R₁ and R₂ is independently selected from the group consisting of H,

- 23 -

wherein $w = 2$ to 6wherein x is 4 to 5

and

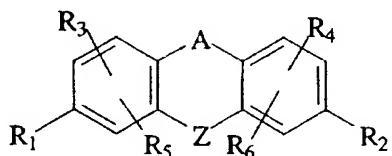
15 $\text{X}-\text{R}_1$, with the proviso that both R_1 and R_2 are not H;
 X is O or S;

- 24 -

each R_3 , R_4 , R_5 , and R_6 is independently selected from the group consisting of -H, -Cl, -Br, -
 20 NO_2 , -CN, -OH, C1 to C8 alkyl, C6 to C8 aryl, C7 to C24 alkylaryl or arylalkyl, C1 to C8 alkoxy, C6 to C18 aryloxy, C7 to C24 alkylaryloxy or arylalkoxy, C1 to C8 alkylthioether, -COOH, and -COOR₁; and

each R_7 , R_8 and R_9 is independently selected from the group consisting of C1 to C8 alkyl and C7 to
 25 C24 alkylaryl or arylalkyl.

17. A method of polymerizing a polymerizable compound comprising at least one ethylenically unsaturated double bond, comprising exposing said compound to ultraviolet radiation in the presence of a
 5 compound having the Formula (I)



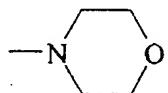
(I)

wherein:

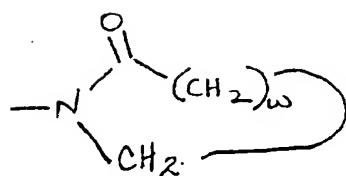
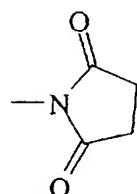
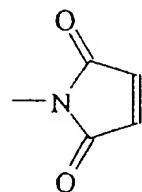
A is -CO- or -CO-CO-;

Z is (H,H), -CH₂- , -S-, -O-, -CO-, -NR₉-, or a bond bridging the two aromatic rings,

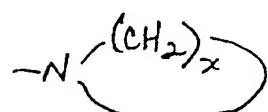
each R_1 and R_2 is independently selected from the group consisting of H,



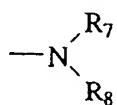
-25-

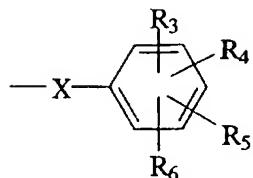
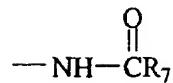


wherein w = 2 to 6



wherein x is 4 to 5





and

$\text{X}-\text{R}_1$, with the proviso that both R_1 and R_2 are not H;

X is O or S;

each R_3 , R_4 , R_5 , and R_6 is independently selected from the group consisting of -H, -Cl, -Br, -NO₂, -CN, -OH, C1 to C8 alkyl, C6 to C8 aryl, C7 to C24 alkylaryl or arylalkyl, C1 to C8 alkoxy, C6 to C18 aryloxy, C7 to C24 alkylaryloxy or arylalkoxy, C1 to C8 alkylthioether, -COOH, and -COOR₁; and

each R_7 , R_8 and R_9 is independently selected from the group consisting of C1 to C8 alkyl and C7 to C24 alkylaryl or arylalkyl.

18. The process of Claim 17, wherein said exposing step comprises exposing said composition to radiation having spectral emphasis in a wavelength band of about 250 to about 350 nanometers (nm).

19. The process of Claim 17, wherein said exposing step comprises exposing said composition to radiation having spectral emphasis in a wavelength band of about 290 to about 325 nm.

20. The process of Claim 17, wherein said exposing step comprises exposing said composition to

-27-

radiation having spectral emphasis in a wavelength band of about 308 nm.

1/5

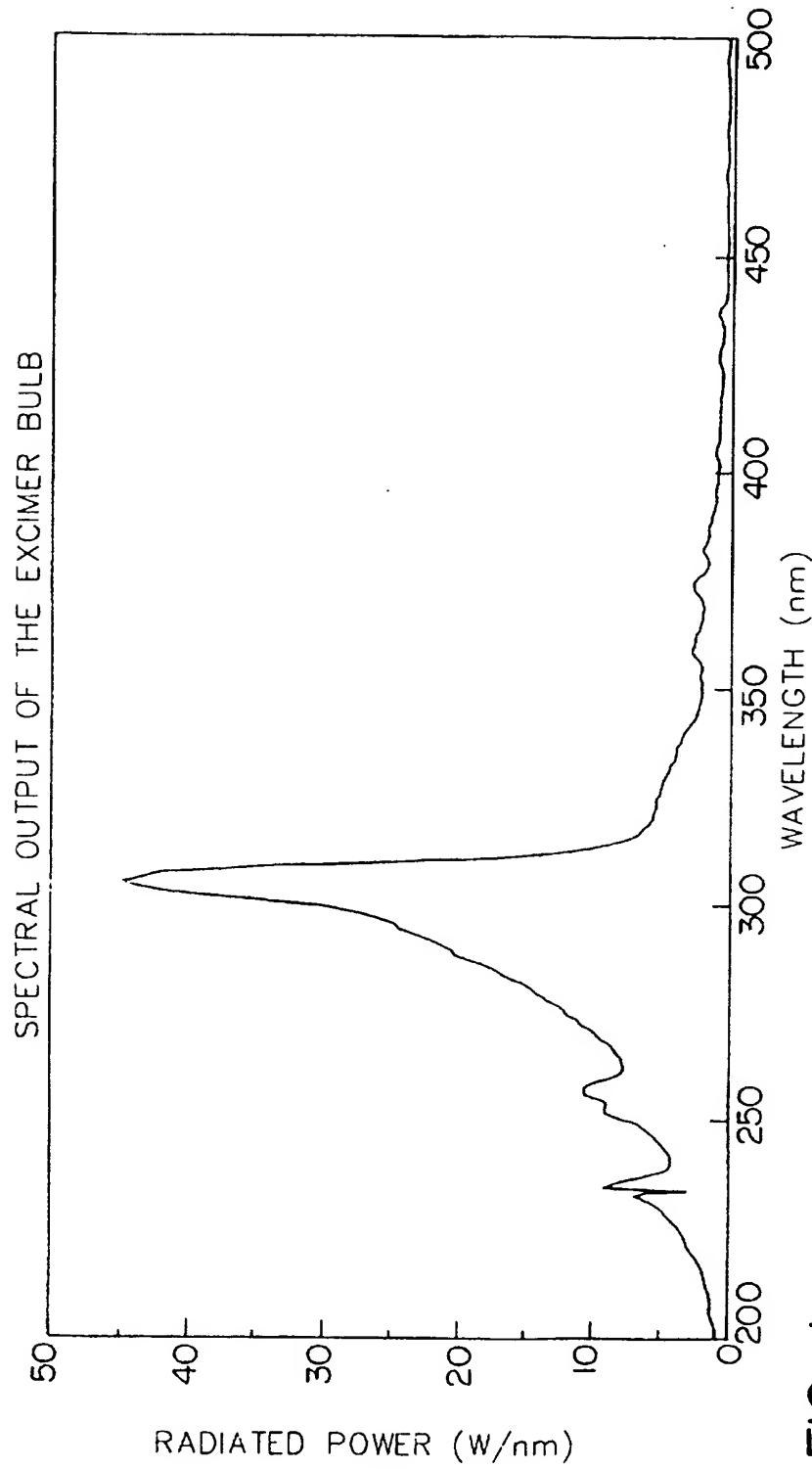


FIG. 1.

2/5

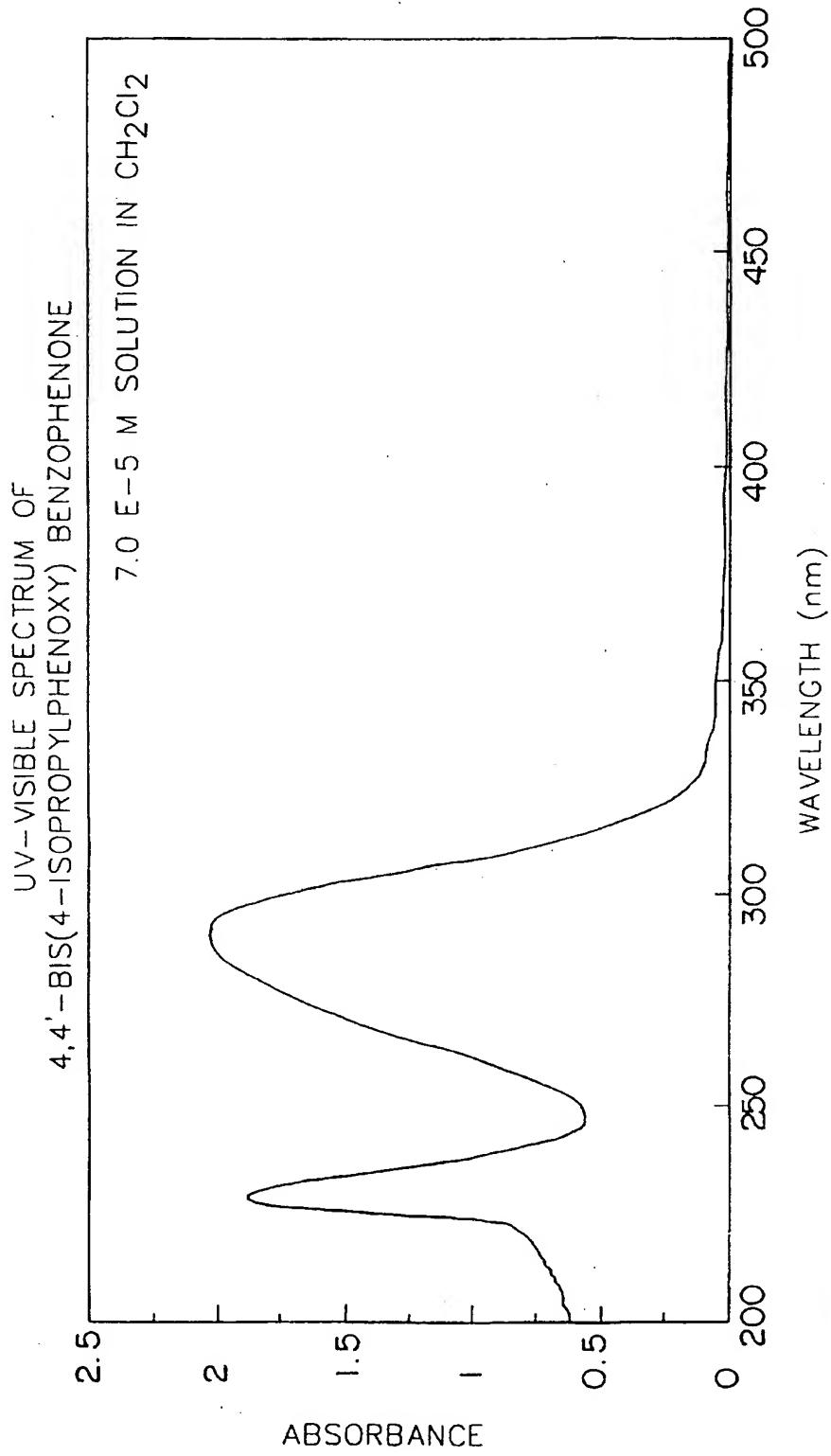


FIG. 2.

3/5

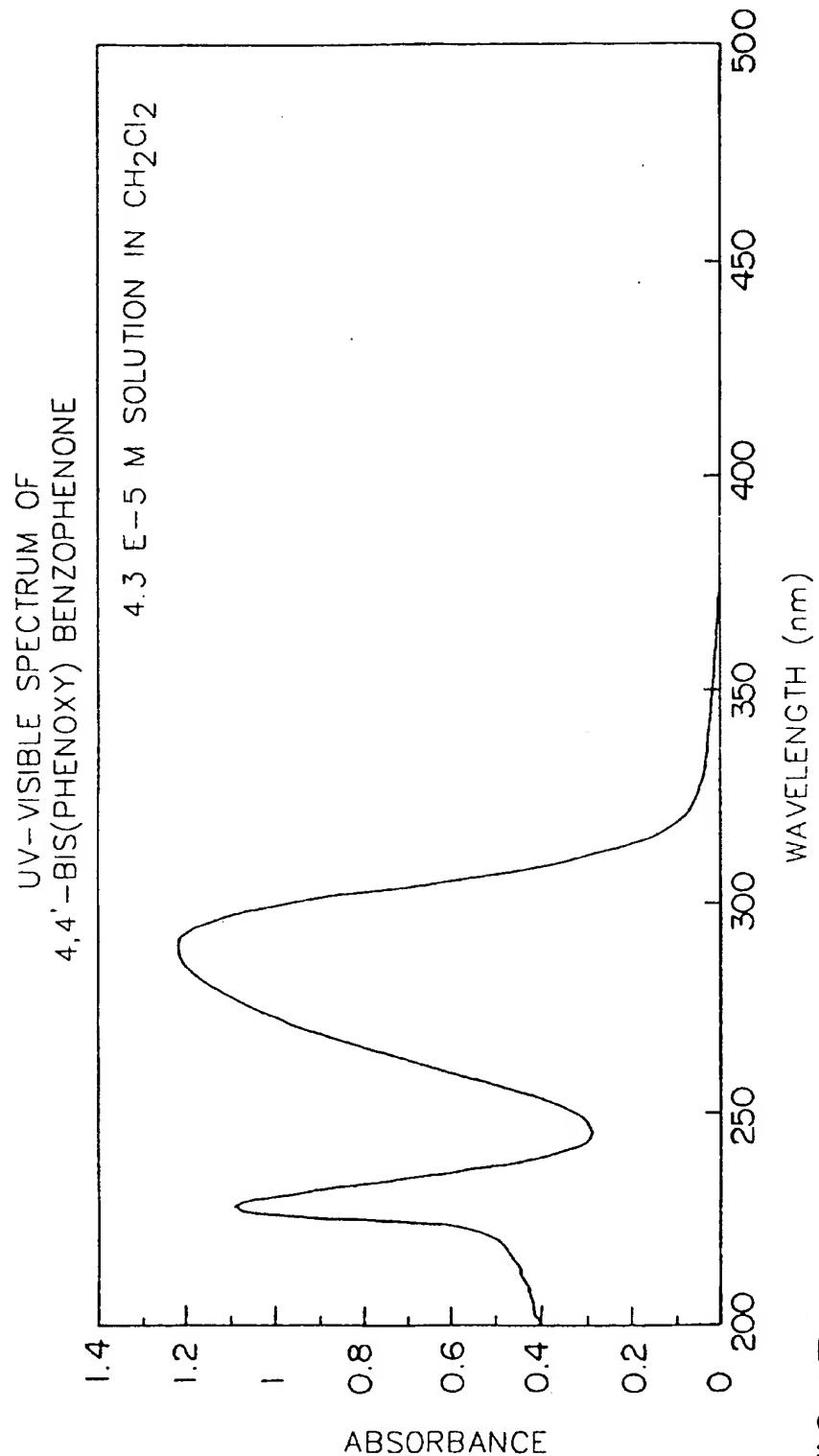


FIG. 3.

4/5

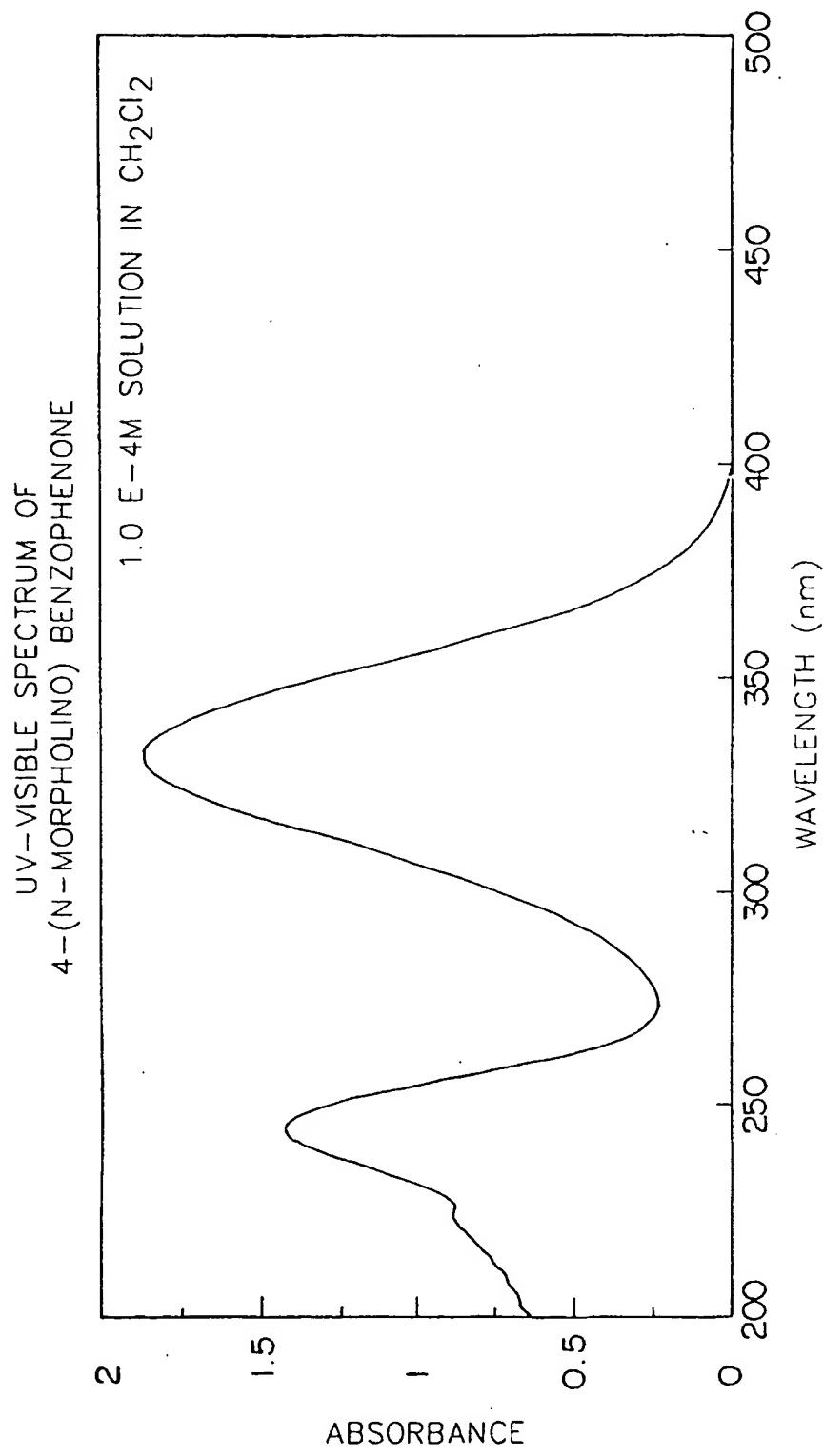


FIG. 4.

5/5

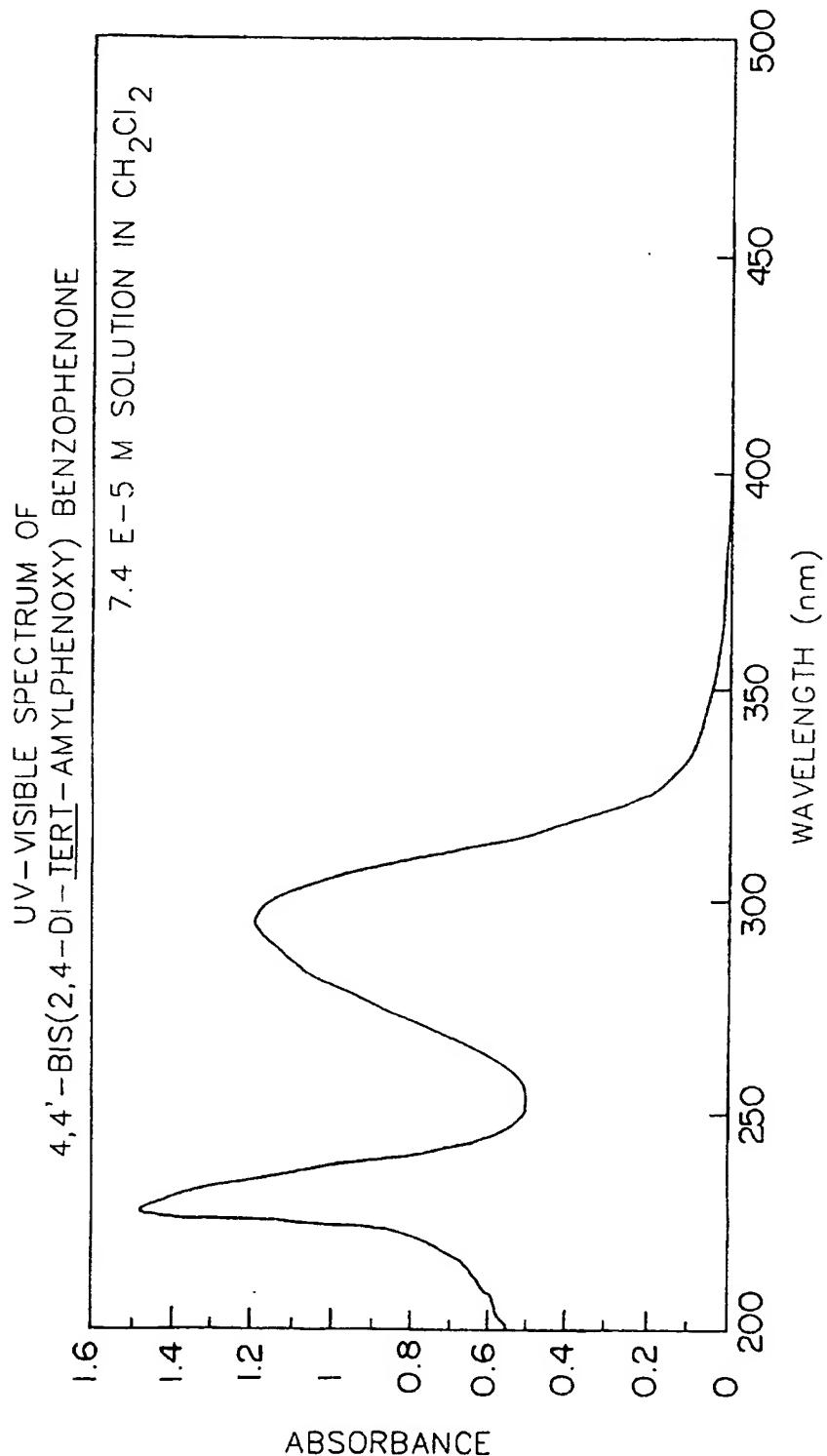


FIG. 5.

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/08512

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08F2/50 G03F7/031 C07D335/16 C07D311/86 C07C49/84

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F G03F C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 150 891 A (THE WELLCOME FOUNDATION LTD.) 7 August 1985 see claim 1 ---	1,2,7,11
X	FR 2 138 875 A (CHEM. PHARMAZ. FABRIK DR. HERMANN THIEMANN GMBH.) 5 January 1973 see claim 1 ---	1,5,6,8, 11
X	GB 2 075 506 A (CIBA-GEIGY AG.) 18 November 1981 see claim 1 ---	16-20
A	US 4 843 179 A (V. JANSONS) 27 June 1989 cited in the application -----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

1

Date of the actual completion of the international search

Date of mailing of the international search report

13 October 1997

28.10.87

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cauwenberg, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/97/08512

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 150891 A	07-08-85	AU 3733885 A		18-07-85
		DK 5785 A		06-07-85
		JP 60222478 A		07-11-85
		US 4623656 A		18-11-86
		US 4616032 A		07-10-86
		US 4737514 A		12-04-88
FR 2138875 A	05-01-73	NONE		
GB 2075506 A	18-11-81	CH 643552 A		15-06-84
		CA 1166635 A		01-05-84
		DE 3117568 A		16-06-82
		FR 2482102 A		13-11-81
		JP 1616026 C		30-08-91
		JP 2038594 B		31-08-90
		JP 57002283 A		07-01-82
		US 4385182 A		24-05-83
US 4843179 A	27-06-89	EP 0323897 A		12-07-89
		JP 1233256 A		19-09-89

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)